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Noble gases, stable isotopes, and radiocarbon as tracers of flow in the Dakota aquifer, Colorado and Kansas

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Abstract

A suite of chemical and isotope tracers (dissolved noble gases, stable isotopes of water, radiocarbon, and Cl) have been analyzed along a flow path in the Dakota aquifer system to determine likely recharge sources, ground water residence times, and the extent of mixing between local and intermediate flow systems, presumably caused by large well screens. Three water types were distinguished with the tracers, each having a very different history. Two of the water types were found in south-eastern Colorado where the Dakota is poorly confined. The tracer data suggest that the first group recharged locally during the last few thousand years and the second group was composed of ground water that recharged earlier during a cooler climate, presumably during the last glacial period (LGP) and mixed aged water. The paleotemperature record archived in this groundwater system indicates that south-eastern Colorado was about 5°C cooler during the LGP than during the late Holocene. Similar temperature changes derived from dissolved noble gases in other aquifer systems have been reported earlier for the south-western United States. The third water type was located down gradient of the first two in the confined Dakota in western and central Kansas. Groundwater residence time of this water mass is on the order of 10⁴–10⁵ yrs and its recharge location is near the Colorado and Kansas border down gradient of the other water types. The study shows the importance of using multiple tracers when investigating ground water systems. © 1998 Elsevier Science B.V. All rights reserved.

Keywords: Isotope hydrology; Paleoclimate; Regional flow system; Dakota aquifer

1. Introduction

Agriculture in the Great Plains region of the United States relies heavily on the availability of groundwater. The High Plains aquifer, which consists of the Ogallala and other hydraulically connected formations, is the dominant source. Declining water levels and degrading water quality in this system pose problems for local users. The underlying Dakota aquifer contains groundwater of sufficient quality in some

areas to supplement the High Plains aquifer. To ensure the long-term viability of this source, managers need to have detailed information of groundwater flow paths, groundwater residence times, and sources of recharge.

The Dakota aquifer and its equivalents underlie much of the Great Plains of the United States. The importance and the lateral extent of this aquifer system has been recognized since the early part of the 20th century (Darton, 1905). Although initially considered to be a classical artesian aquifer (Darton, 1905), recent investigations suggest a complex

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hydrologic system (Helgesen et al., 1982; 1993; Belitz and Bredehoeft, 1988; Macfarlane, 1995). By using measurements of hydraulic heads and numerical simulations of flow, these studies have shown that rock outcrops along the western margin of the Denver Basin are not hydraulically connected with the aquifer system lying down-dip to the east. Belitz and Bredehoeft (1988) and Macfarlane (1995) have also suggested that the regional flow system is influenced by the thickness of the overlying aquitards and surface drainage basins which have cut down into the Dakota. Both influences act to partially isolate the Dakota from sources of recharge resulting in subhydrostatic pressures in the confined aquifer.

Chemical and isotope tracers provide additional information which can be used with hydraulic head data and numerical calculations to verify and refine subsurface flow patterns. Each tracer has its strengths and weaknesses. Thus, the most reliable approach is to use a suite of tracers (Phillips, 1995). In this study, we examined the flow system along a flow path in the Dakota aquifer which extends from south-eastern Colorado to central Kansas using noble gases, stable isotopes of water ($^{18}\text{O}/^{16}\text{O}$ and D/H), carbon isotopes ($^{14}\text{C}/^{12}\text{C}$ and $^{13}\text{C}/^{12}\text{C}$) of dissolved inorganic carbon (DIC), and chloride (Cl).

1.1. Chemical and isotope tracers

Carbon isotopes of DIC and stable isotopes of water have been used frequently as groundwater tracers (e.g. Pearson and White, 1967; Winograd and Friedman, 1972; Rozanski, 1985; Phillips et al., 1986; 1989; Siegel, 1991; Davisson and Criss, 1993; Dutton, 1995; Rose and Davisson, 1996). ^{14}C is the most reliable chronometer of moderately old groundwater (5–30 kyr) although corrections must be made to account for water–rock interactions. Stable isotopes have been used to identify possible recharge areas and mixing within aquifer systems. However, in regional studies, interpretations of stable isotopes are more complicated because their input functions vary with a number of different factors including elevation, precipitation amount, continentality, and long term climate change (Dansgaard, 1964; Rozanski, 1985; Clark et al., 1997). Noble gases have been used sparingly as groundwater tracers. Yet when combined with other isotope and chemical tracer data, they provide

valuable information about groundwater flow and residence times (e.g. Blavoux et al., 1991; Clark et al., 1997).

Concentrations of dissolved noble gases (He, Ne, Ar, Kr, and Xe) in groundwater reflect a number of different processes. In the recharge area, their concentrations are set by: (1) solubility equilibrium with the soil air at in situ temperatures; and (2) dissolution of trapped air bubbles which form as a result of fluctuations of the water table. The latter source has been termed the excess air component (Heaton and Vogel, 1981). As groundwater flows away from the recharge area, it can no longer exchange with the soil air and, in relatively young groundwater (< 100 kyr), concentrations of the heavier noble gases (Ne, Ar, Kr, and Xe) remain unchanged. However, the concentration of ^4He increases with time as a result of the α -decay of U- and Th-series nuclides both within the aquifer rock and deeper in the crust (e.g. Bottomley et al., 1984; Torgersen and Ivey, 1985; Stute et al., 1992b). In rare cases, He of mantle origin can also accumulate (e.g. Stute et al., 1992b; Torgersen et al., 1995). Thus, ^4He concentrations can be used as an approximate chronometer.

Recharge temperatures are calculated from concentrations of Ne, Ar, Kr, and Xe after correcting for excess air (Stute and Schlosser, 1993; Stute et al., 1995b), using solubility equilibrium data (Weiss, 1970; 1971; Clever, 1979) and the inferred elevation of the recharge area. This method can easily resolve the temperature change between the climates of the Holocene and the last glacial period (LGP), and has become an important tool for reconstructing continental temperatures of past climates (e.g. Andrews and Lee, 1979; Stute and Deak, 1989; Stute et al., 1992a; b; 1995a and b). These studies have also shown that noble gas temperatures of young water (<10 kyr) are identical to modern mean annual soil temperatures, which in the United States are typically 0–2°C more than mean annual air temperatures (Smith et al., 1964).

Detailed paleotemperature records have been determined from three aquifers in the southern and western United States. The records are from the Carrizo aquifer in south Texas, the San Juan Basin in north-western New Mexico, and the Floridan aquifer in south-eastern Georgia (Stute et al., 1992a and b; 1995a; Clark et al., 1997). These records have shown that this broad region was 4–6°C cooler during the LGP

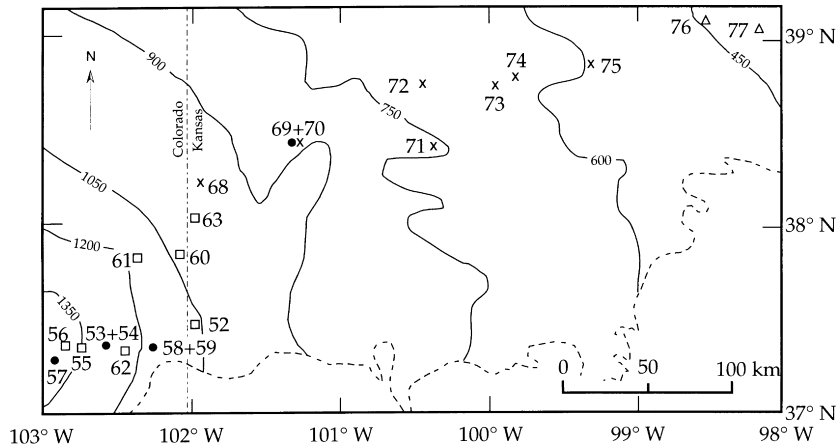


Fig. 1. Map of the well locations (symbols with KGS no.), elevation of the predevelopment potentiometric surface (m above sea level; solid line) and the southern extent of the Dakota aquifer system (dashed line) in south-eastern Colorado and western Kansas. The following symbols are used to distinguished the different water types (see the text and Table 3): Group no. 1, filled circles; Group no. 2, open squares; Group no. 3, crosses; and other, open triangles.

than during the Holocene and that the inland (altitude) temperature gradient between Texas (elevation = 200 m) and New Mexico (elevation = 2000 m) was about the same during these two periods.

1.2. Study area

Samples were collected along a flow path which extends from south-eastern Colorado to central

Kansas (Fig. 1). The land surface in this part of the High Plains slopes eastward from more than 1500 m in south-eastern Colorado to less than 500 m in central Kansas. Three major drainage basins of the Arkansas, the Smoky Hill, and the Saline Rivers lie within the study area and locally increase the topographic relief.

Mean annual air temperatures vary with elevation and latitude in this part of the High Plains. The regional altitude and latitudinal temperature gradients are

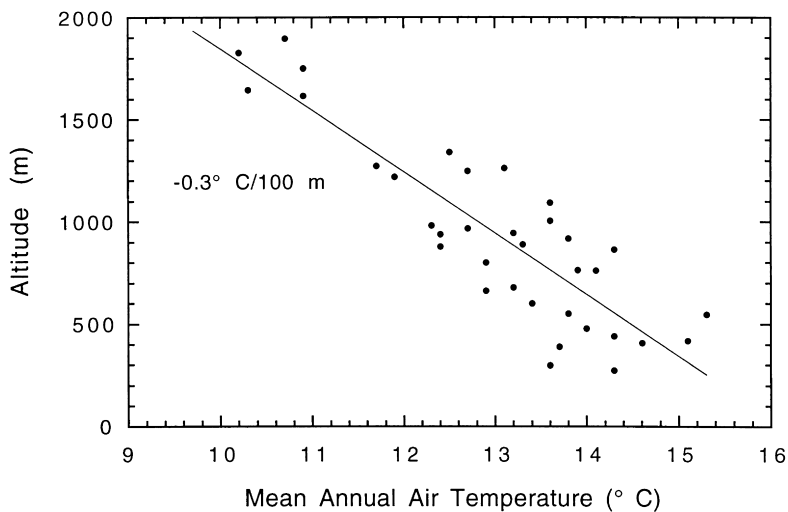


Fig. 2. Mean annual air temperature from weather stations in the study area (south-eastern Colorado and western Kansas) plotted as a function of land surface elevation. Mean annual air temperature decreases with elevation at rate of 0.3°C per 100 m of elevation gain.

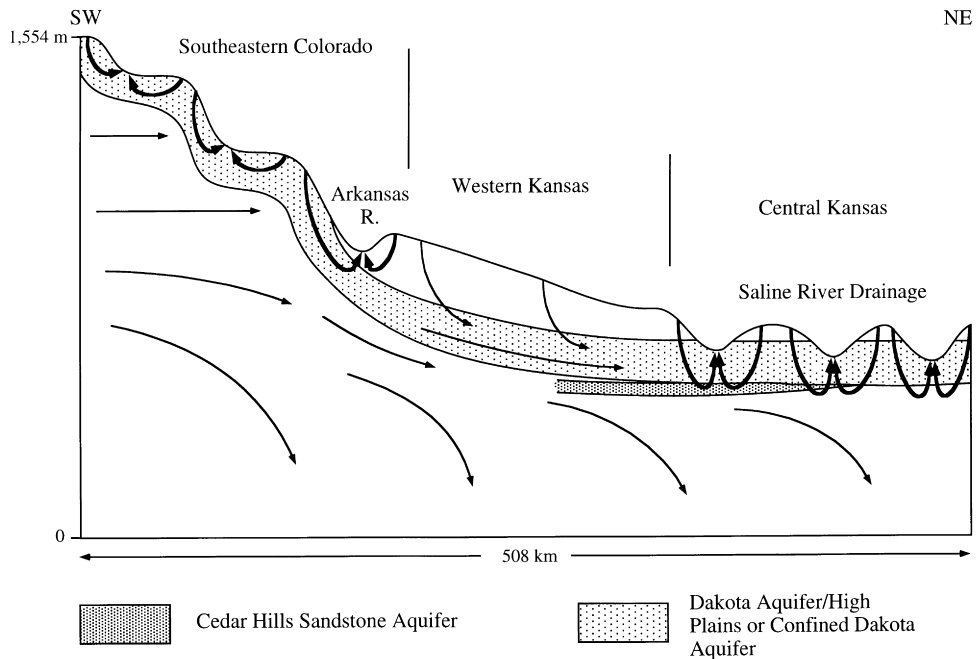


Fig. 3. Conceptual model of groundwater flow through the Dakota aquifer in south-eastern Colorado and western Kansas. Most of the recharge to the Dakota occurs in south-eastern Colorado and central Kansas is routed back to the surface by local flow systems (Macfarlane, 1995).

about -0.3°C per 100 m (Fig. 2) and -0.8°C per degree latitude. Because the slope of the land surface elevation is small, large longitudinal sections of the study area are nearly isothermal. For instance, the present day 30-year mean annual air temperature at stations near the Colorado–Kansas border south of the Arkansas River (101°W – 103°W and 37°N – 38°N) is $12.5 \pm 0.6^{\circ}\text{C}$. More than half of the wells sampled in this study lie there. The most rapid increase in elevation and decrease in temperature occurs to the west of this area where the topographic slope increases.

The majority of the samples examined in this study were collected from the Dakota aquifer system. This system covers two-thirds of the state of Kansas, and nearly all of Nebraska and eastern Colorado and consists of a sequence of interbedded marine and non-marine Cretaceous sandstones and mudstones with a total thickness that can exceed 200 m in some areas. The sandstones occur as discontinuous permeable bodies within relatively impervious shaley strata and generally occur in several distinct zones.

In eastern Colorado and Kansas, flow in the Dakota aquifer is influenced primarily by regional and local

topography and the thickness of the Upper Cretaceous aquitard (Macfarlane, 1995). The water table or the top of the zone of saturation mimics the topography, leading to an easterly flow of groundwater (Fig. 1). In north-west Kansas where the aquitard is thickest, hydraulic heads in the Dakota are more than 90 m lower than would be expected in a flow system that is in good hydraulic connection with the overlying water table. This is due to the low permeability and great thickness of the aquitard (Helgesen et al., 1993). However, to the south and east the reduced aquitard thickness brings the Dakota closer to the surface. The resulting expansion of the shales due to unloading from erosion may have significantly increased the aquitard's permeability (Neuzil and Pollock, 1983; Neuzil, 1993). Here, local topography is the dominant influence on groundwater flow and the Dakota receives more local recharge.

Most of the recharge to the Dakota aquifer system occurs via two paths: (1) direct recharge in outcrop areas; and (2) seepage from the overlying High Plains aquifer where the two systems are hydraulically connected. The dominant area of freshwater recharge

Table 1
Well data and chemical results

KGIS no.	Latitude (°W)	Longitude (°N)	Formation ^a	Elevation (m asl)	Depth (m asl)	Temp (°C)	pH	Ca (meq l ⁻¹)	Mg (meq l ⁻¹)	K (meq l ⁻¹)	Na (meq l ⁻¹)	Cl (meq l ⁻¹)	HCO ₃ (meq l ⁻¹)	SO ₄ (meq l ⁻¹)	SiO ₂ (meq l ⁻¹)
Group no. 1 Wells															
53	102.61	37.36	HP, Dak	1345	1235	15.1	7.7	4.03	1.33	0.08	0.60	0.71	2.23	2.83	0.69
54	102.62	37.38	Dak	1330	1268	14.8	7.3	4.22	1.47	0.09	1.99	0.58	2.79	4.46	0.57
57	102.95	37.28	Dak	1505	–	15.9	7.5	2.86	0.85	0.07	0.30	0.22	3.25	0.35	0.78
58	102.29	37.37	Dak	1210	1143	16.1	7.6	4.42	4.63	0.08	4.57	1.39	4.05	7.46	0.58
59	102.28	37.37	Dak	1200	1139	16.1	7.6	3.14	2.99	0.09	2.90	0.63	3.93	4.13	0.64
69	101.36	38.45	HP	1005	955	15.3	7.7	2.66	1.86	0.12	0.83	0.87	3.54	0.84	1.95
Group no. 2 Wells															
52	102.02	37.50	Mor	1090	964	16.5	8.2	2.19	2.21	0.22	3.61	0.57	3.87	3.83	0.54
55	102.77	37.35	Dak	1420	1338	16.0	7.5	2.42	2.51	0.26	4.52	0.67	4.41	4.52	0.30
56	102.85	37.38	Dak	1450	1337	16.7	7.1	1.75	1.04	0.08	0.64	0.07	2.74	0.60	0.41
60	102.16	37.85	Dak	1100	–	19.3	7.4	2.94	1.37	0.10	1.03	0.21	3.02	2.08	0.55
61	102.37	37.83	Dak	1190	1013	16.8	7.1	3.13	1.79	0.10	1.46	0.26	3.67	2.52	0.49
62	102.46	37.36	Dak, Mor	1270	1177	16.5	7.6	1.87	1.51	0.11	1.79	0.15	3.84	1.15	0.39
63	102.01	38.05	Dak	1020	910	17.4	7.3	3.22	1.78	0.16	1.99	0.34	3.23	3.40	0.37
Group no. 3 Wells															
68	101.95	38.25	Dak	1105	793	24.3	8.4	0.15	0.12	0.09	7.48	0.47	4.59	2.46	0.41
70	101.36	38.45	Dak	1005	645	24.5	8.5	0.27	0.21	0.12	16.0	1.79	5.66	8.77	0.41
71	100.40	38.45	Dak	810	528	24.4	7.7	0.91	0.67	0.18	15.3	8.46	5.57	0.51	
72	100.44	38.75	Dak	760	547	24.5	8.2	0.20	0.16	0.11	15.0	4.74	6.30	4.40	0.39
73	99.96	38.75	Dak	725	530	20.6	7.9	0.36	0.28	0.10	16.6	7.84	5.84	0.39	
74	99.76	38.80	Dak	660	516	20.3	8.3	0.27	0.25	0.15	20.9	10.3	7.25	4.08	0.37
75	99.31	38.95	Dak	640	486	20.3	7.9	0.78	1.69	0.28	50.4	38.5	6.34	0.41	
Other Wells															
76	98.49	39.10	Dak	515	444	16.5	8.1	1.05	0.35	0.09	14.1	2.82	8.97	3.31	0.31
77	98.15	39.07	Dak	440	416	15.1	7.1	8.65	1.01	0.15	2.71	1.65	6.21	2.67	0.81

^a HP = High Plains aquifer; Dak = Dakota aquifer; Mor = Morrison aquifer

Table 2
Isotope and chemical tracer results

KGS no.	$\delta^{13}\text{C}$ (‰)	^{14}C (pme)	Age ^a (kyr)	$\delta^{18}\text{O}$ (‰)	δD (‰)	$^3\text{H}^b$ (TU)	He (cc STP g ⁻¹) (10 ⁻⁸)	Ne (cc STP g ⁻¹) (10 ⁻⁷)	Ar (cc STP g ⁻¹) (10 ⁻⁴)	Kr (cc STP g ⁻¹) (10 ⁻⁵)	Xe (cc STP g ⁻¹) (10 ⁻⁸)	Recharge elevation (m)	Excess air (cc STP g ⁻¹) (10 ⁻³)	T _{avg} (°C)	T _{Ne}	T _{Ar}	T _{Kr}	T _{Xe}	F _{Ne} ^c
Group no. 1 Wells																			
53	-3.0	81.1	0.4	-11.4	-85	4.0	4.04	1.69	2.96	6.85	0.97	1400	0.3	14.5	14.8	14.4	14.3	1	
54	-5.4	74.4	1.1	-10.7	-75	4.8	4.85	1.77	3.06	7.17	1.00	1400	0.6	13.3	13.8	12.9	13.3	1	
57	-5.2	75.0	1.0	-9.8	-67	0	-	-	-	-	-	-	-	-	-	-	-	-	-
58	-7.4	72.4	1.3	-9.4	-68	0.1	6.58	1.81	3.12	7.20	1.00	1400	0.9	13.1	13.2	12.9	13.3	1	
59	-6.2	68.2	1.8	-9.7	-66	3.0	6.75	1.82	3.11	7.22	1.02	1400	0.9	13.1	13.4	12.9	12.9	1	
69	-8.1	70.9	1.5	-8.9	-61	3.1	4.54	1.79	3.19	7.45	1.03	1100	0.5	13.1	13.1	12.7	13.5	1	
Group no. 2 Wells																			
52	-6.6	17.9	12.9	-10.9	-79	1.0	38.0	3.40	4.43	9.45	1.25	1200	-	10.6	10.6	10.7	10.5	10.7	0.41
55	-4.9	27.8	9.2	-4.1	-104	0	49.4	2.07	3.79	8.66	1.15	1800	-	-	-	-	-	-	0.01
56	-5.7	40.6	6.1	-11.5	-80	0	10.1	2.52	3.64	8.21	1.28	1800	-	7.7	7.8	8.9	8.65	8	0.96
60	-7.7	37.5	6.8	-9.2	-60	0	10.3	2.13	3.43	7.84	1.09	1200	-	11.7	11.7	11.5	11.9	0.96	
61	-8.6	44.6	5.3	-10.0	-69	0	-	-	-	-	-	-	-	-	-	-	-	-	-
62	-6.3	21.6	11.3	-12.2	-88	-	29.7	2.28	3.56	8.42	1.26	1800	-	7.1	7.1	8.2	7.0	6.0	0.96
63	-4.5	35.7	7.2	-13.0	-93	0	40.3	2.23	3.75	8.82	1.35	1200	-	6.9	6.9	7.7	7.4	5.7	0.96
Group no. 3 Wells																			
68	-9.0	1.2	35.6	-13.2	-99	0.4	167	2.21	3.76	8.77	1.17	1200	-	-	-	-	-	-	0.06
70	-8.4	0.5	42.1	-12.1	-90	0	318	2.15	3.58	8.00	1.03	1100	-	-	-	-	-	-	0.01
71	-5.1	14.9	14.4	-12.5	-95	0.1	573	1.89	3.55	8.35	1.13	1100	-	-	-	-	-	-	0.01
72	-6.4	5.6	22.5	-11.8	-97	0	890	1.93	3.42	8.08	1.09	1100	-	-	-	-	-	-	0.01
73	-4.1	0.2	51.4	-12.0	-87	0	661	2.37	3.70	8.42	1.11	1100	-	-	-	-	-	-	0.01
74	-6.5	1.3	34.7	-11.9	-88	0	1090	1.89	3.47	8.04	1.05	1100	-	-	-	-	-	-	0.01
75	-7.3	1.7	32.5	-11.7	-88	0	3630	1.83	3.34	7.75	1.06	1100	-	-	-	-	-	-	0.01
Other Wells																			
76	-8.0	18.8	12.5	-9.3	-64	4.7	125	2.30	3.94	9.36	1.46	700	-	6.7	6.7	7.7	7.2	5.3	0.96
77	-8.0	80.0	0.5	-8.5	-61	2.8	19.0	2.18	3.70	8.47	1.16	500	1.9	11.6	1.6	11.2	11.3	12.3	1
σ	± 0.3	± 1		± 0.1	± 1	± 1	$\pm 2\%$	$\pm 2\%$	$\pm 1\%$	$\pm 1\%$	$\pm 1\%$			± 1					

^a Ages calculated using the model of Vogel (1970)

^b Tritium values have been blank corrected.

^c Fraction of excess Ne that degassed after formation ($F_{\text{Ne}} = ([\text{Ne}]_{\text{tot}} - [\text{Ne}]_{\text{iso}})_{\text{final}} / ([\text{Ne}]_{\text{tot}} - [\text{Ne}]_{\text{iso}})_{\text{initial}}$; see Stute et al., 1995b)

is in the topographically elevated region of south-eastern Colorado, south of the Arkansas River where the Dakota crops out at the surface and subcrops beneath the High Plains aquifer. In central Kansas, the Dakota receives saline water from the underlying Cedar Hills Sandstone where both aquifers are hydraulically connected (Fig. 3).

Numerical modeling of the Dakota flow system suggests that only about 10% of the infiltrated water entering the aquifer in south-eastern Colorado moves down gradient into the confined Dakota in western Kansas (Macfarlane, 1995). The rest is discharged into surface streams near the recharge area. The primary discharge areas for the confined Dakota aquifer are in the river valley systems in central Kansas (Macfarlane, 1995).

The chemical character and quality of groundwater in the Dakota aquifer ranges widely from Ca–HCO₃ to Na–Cl–HCO₃ and Na–Cl waters. The latter type is usually found in the eastern and northern portions of the aquifer where the underlying confining units that separate the Dakota from salt water aquifers are thin (Macfarlane et al., 1990). Whittemore and Fabryka-Martin (1992) characterized the Cl–Br and Cl–I ratios of the Dakota groundwaters and showed that the high Cl concentration are related principally to the upward migration of fluids which have been in contact with halite.

2. Methods

Samples were collected from 17 wells open to the Dakota aquifer (Table 1) along a flow path which extended for more than 450 km from south-eastern Colorado (el. 1400 m) to central Kansas (el. 400 m). One sample was collected from the overlying Ogallala aquifer (KGS no. 69) and one sample was collected from the underlying Morrison aquifer (KGS no. 52) midway down the flow path. Nine of the samples were collected from municipal wells, and the remainder were collected from either domestic or agricultural wells equipped with submersible pumps or windmills (KGS no. 57 and 61).

Noble gas samples were collected in 10 ml copper tubes at all wells except for those with windmills. At the outlet end of the tube, Tygon tubing and a regulator valve were attached. The water pressure was

raised by reducing the flow through the valve until no bubbles were detected in the Tygon. After thoroughly flushing at high pressure, the copper tubes were sealed at each end with steel pinch-off clamps.

Groundwater temperatures, conductivities, and pHs were measured in the field at the wellhead. Samples for major and minor chemical analyses were filtered (0.45 µm filter paper) and collected in Nalgene plastic bottles and samples for the stable isotopes of water (¹⁸O/¹⁶O and D/H), tritium, and carbon isotopes of DIC (¹⁴C/¹²C and ¹³C/¹²C) were collected in 1 l glass bottles with air-tight caps. The carbon isotope sample was preserved by adding about 0.5 ml of HgCl₂ solution.

2.1. Laboratory Analysis

The major and minor elemental analyses were completed by the Analytical Services Section at the Kansas Geological Survey using standard atomic adsorption and ion chromatographic techniques (Table 1). All isotopic analyses were completed through the Isotope Sciences Division at Lawrence Livermore National Laboratory (Table 2). Stable isotopes of water were determined using the CO₂ equilibration method for ¹⁸O/¹⁶O ratios (Epstein and Mayeda, 1953) and the zinc-reduction method for D/H ratios (Coleman et al., 1982), followed by analysis on an isotope ratio mass spectrometer. Analyses are reported in the standard δ notation representing per mil deviations from the SMOW standard (Standard Mean Ocean Water; Craig, 1961), and reproducibility is ± 0.1‰ for the δ¹⁸O analyses and ± 1.0‰ for the δD analyses. Tritium, which is reported in tritium units (TU), was measured by a ³He accumulation method (Surano et al., 1992), where the samples were vacuum degassed and shelved for 60 days to allow for the growth of ³He from tritium decay. Blank levels are approximately 1 TU with a reproducibility of ± 1 TU.

DIC was extracted from each sample by adding 1 ml of 100% phosphoric acid and vacuum stripping of the water. The CO₂ liberated was cryogenically trapped, separated from water vapor, and split for ¹³C and ¹⁴C analyses. ¹³C/¹²C ratios were determined on a mass spectrometry and ¹⁴C contents were determined by accelerator mass spectrometry after the CO₂ gas had been reduced to graphite. ¹³C analyses are

Table 3

Summary of the characteristic tracer composition of the three groups of samples found in the Dakota Aquifer

	Group no. 1	Group no. 2	Group no. 3
Geographical location	SE CO + W KS	SE CO + W KS	Central KS
KGS Well no.	53, 54, 57, 58, 59, 69	52, 55, 56, 60, 61, 62, 63	68, 70, 71, 72, 73, 74, 75
¹⁴ C content (pmc)	> 70	18 to 45	< 5
¹⁴ C model age (kyr)	< 2	6 to 13	> 20
T _{ng} (°C)	13.1 to 14.5	6.9 to 11.7	–
δ ¹⁸ O (‰)	– 9 to –11	– 9 to –14	– 12
Cl (meq l ⁻¹)	0.2 to 1.4	0.2 to 0.7	2 to 39
He (10 ⁻⁸ cc STP gr ⁻¹)	4 to 7	10 to 50	170 to 3600

reported as δ values relative to the PDB standard and ¹⁴C abundances are reported as percent modern carbon (pmc). Reproducibilities for the ¹⁴C are ± 1pmc, and the δ¹³C is ± 0.3‰.

Noble gas concentrations were determined on a Nuclide 6-60 noble gas mass spectrometer using an isotope dilution method. The copper tubes were connected to a high vacuum extraction-clean-up system in the laboratory. Prior to extracting the noble gases from water samples, a constant volume of an isotope spike mixture was released into an isolated portion of the vacuum system. In the same location, noble gases were extracted from the water sample with three boil–freeze cycles. In addition to extracting more than 99% of the dissolved noble gases from the water, these cycles helped to mix the spike and sample. Noble gases were separated from other gases by a series of cold traps and titanium getters. The system was calibrated using equilibrated water samples (at known temperatures, approximately 21°C) and known volumes of air. Absolute concentrations were determined with a precision of ± 1% and ± 2% for the heavier noble gases (Ne, Ar, Kr, and Xe) and He, respectively.

2.2. Excess air correction

In order to estimate recharge temperatures, noble gas concentrations need to be corrected for excess air. In these calculations, the salinity effect on noble gas concentrations was not explicitly calculated because the salinity of the recharging water was low (< 500 ppm) and the salinity effect is negligible. Previous studies have shown that the noble gas composition of excess air is frequently the same as the atmosphere (Andrews and Lee, 1979; Stute and

Deák, 1989; Stute et al., 1992a; b; 1995a). When this is the case, recharge temperatures can be calculated using an iterative method described by Stute and Schlosser (1993). Of the 19 wells sampled during this study, noble gas recharge temperatures could be calculated for only 6 assuming that the composition of the excess air component was similar to that of the atmosphere. Poor agreement was found between the calculated recharge temperature for each noble gas for the other 13 samples indicating that the excess air component was fractionated. Fractionated excess air has been found in other aquifer systems (Stute et al., 1995b; Clark et al., 1997). In these cases, it was assumed that a portion of the excess air was lost due to gas transfer across the water table after formation and recharge temperatures were calculated using the method outlined by Stute et al. (1995b).

The recharge elevations were estimated by examining detailed potentiometric maps and determining likely flow paths from areas of recharge to sampled wells (Table 2). Noble gas partial pressures were corrected for the differences in elevation of recharge prior to calculating noble gas temperatures. The uncertainty of the noble gas recharge temperature is ± 1°C.

3. Results

Seventeen of the 19 wells sampled in this study can be split into three groups based on the chemical and isotope tracer data (Table 2 and Table 3). These distinct water bodies are found in different portions of the aquifer system along the flow path. Two of the water bodies are found in extreme western Kansas and south-eastern Colorado in the regional recharge area

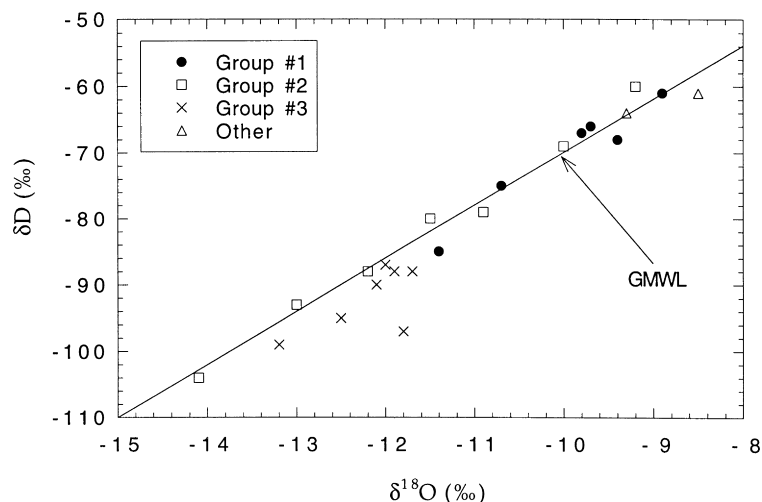


Fig. 4. Plot of δD vs $\delta^{18}O$. The global meteoric water line (GMWL) has been plotted for reference.

for the Dakota and the third is found in central Kansas in the confined aquifer.

Samples collected from Group no. 1 wells (KGS nos 53, 54, 58, 59, 69) are characterized by ^{14}C values greater than 70 pmc and noble gas temperatures which range between 13.1°C and 14.5°C (mean = $13.4 \pm 0.6^\circ C$). The high ^{14}C content indicates that these waters are at most a few thousand years old and thus they represent water that was recharged during the late Holocene. The presence of tritium in all but one sample suggests that they contain a fraction that must have recharged during the last 40 yrs. The noble gas temperatures are in good agreement with the local present day mean annual air temperature, $12.5 \pm 0.6^\circ C$, which tends to be 0–2°C less than the mean annual soil temperature (Smith et al., 1964). Good agreement between the recharge temperature of each of the heavier noble gases was found assuming the composition of excess air was the same as that of the atmosphere. These samples were also characterized by low He and Cl concentrations.

KGS no. 77, which lies at the down gradient end of the flow path in central Kansas, has some of the characteristics of the Group no. 1 samples. While its ^{14}C content and He concentration were similar, it had a noble gas temperature, 12.2°C, slightly cooler and a Cl concentration about 5 times greater than the Group no. 1 samples. KGS no. 77 lies significantly north, where the present day mean annual temperature is

slightly cooler. Thus, its noble gas temperature reflects the local mean annual air temperature, a characteristic of the Group no. 1 samples.

Values of $\delta^{13}C$, $\delta^{18}O$, and δD vary considerably in the Group no. 1 and KGS no. 77 samples, although $\delta^{18}O$ and δD vary systematically along the flowpath. A plot of $\delta^{18}O$ against δD shows that these samples fall close to the global meteoric water line (Fig. 4). Values of $\delta^{18}O$ decrease from -8.5‰ at the down gradient end (KGS no. 77, el. 440 m) to -11.4‰ at the up-gradient end (KGS no. 53, el. 1345 m) with most of the decrease occurring up-gradient of KGS no. 69 (el. 1005 m; $\delta^{18}O = -8.9\text{‰}$). There is a very weak correlation between the composition of $\delta^{18}O$ and elevation above 1000 m with the more depleted groundwater found at higher elevations. Unlike $\delta^{18}O$ and δD , $\delta^{13}C$ does not exhibit any trend with well location. Furthermore, $\delta^{13}C$ values do not correlate with either ^{14}C content or $\sum CO_2$ concentration.

Group no. 2 well samples (KGS no. 52, 55, 56, 60, 62, and 63) have ^{14}C contents between 45 and 17 pmc and noble gas temperatures between 4.8°C and 11.7°C. They are found in the same region (the regional recharge area) as the Group no. 1 wells and have overlapping depths, but are drilled, on average, deeper into the aquifer. Except for KGS no. 52, these samples do not contain tritium. The tritium content of KGS no. 52, 1 ± 1 TU, suggests that this sample contains a

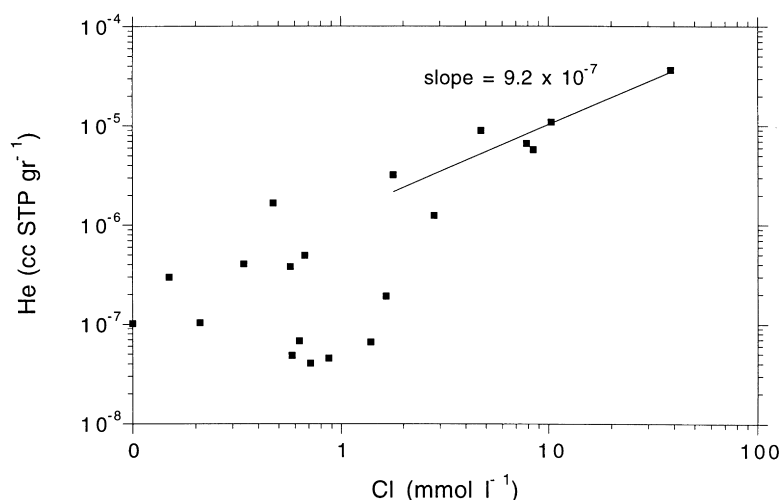


Fig. 5. He concentration plotted as a function of Cl concentration. Only samples with He concentration greater than 10^{-6} cc STP g^{-1} were used in calculating the linear fit of the data.

fraction of groundwater which recharged during the last 40 years. The noble gas data indicate that the excess air composition was fractionated relative to the atmosphere. Hence, the noble gas temperatures were calculated using the fractionation model developed by Stute et al. (1995b). The model works well for most of these samples. However, the results for KGS no. 55 suggests that 99% of the initially dissolved excess air fraction subsequently degassed. This seems unlikely and suggests that other mechanisms not explicitly accounted for by the model of Stute et al. (1995b) are occurring. Hence, a noble gas temperature was not calculated for this sample.

He concentrations in the Group no. 2 samples are about an order of magnitude higher than the Group no. 1 samples and Cl concentrations are slightly lower. The higher He concentrations and lower ^{14}C content indicate that the groundwater ages of the Group no. 2 wells are older than that of the Group no. 1 wells. Macfarlane et al. (1997) have argued that the lower Cl concentrations in the Group no. 2 samples are indicative of higher recharge rates that occurred during this earlier period. As is the case with the Group no. 1 samples, $\delta^{18}\text{O}$ and δD values fall along the global meteoric water line. $\delta^{18}\text{O}$ values are, on average, 2‰ lighter than the Group no. 1 samples and range between -14.1% and -9.2% . They do not correlate strongly with elevation of well-head.

Group no. 3 well samples (KGS no. 68, 70, 71, 72,

73, 74 and 75) have ^{14}C contents less than 15 pmc and are located down-gradient from both the Group no. 1 and no. 2 wells in western and central Kansas. Their He and Cl concentrations are significantly greater than the other groups and, with the exception of KGS no. 68, their $\delta^{18}\text{O}$ and δD values display a much narrower range ($-12.5\% < \delta^{18}\text{O} < -11.7\%$). As with KGS no. 55, noble gas temperatures could not be calculated with either excess air model suggesting that fractionation processes in addition to degassing has affected these samples.

Absolute ^{14}C ages are difficult to calculate for the sampled wells using standard correction methods because of the $\delta^{13}\text{C}$ range found in the young groundwater ($^{14}\text{C} > 68$ pmc). For instance, the isotopic composition of the DIC from KGS no. 53 ($\delta^{13}\text{C} = -3.0\%$ and $^{14}\text{C} = 81$ pmc) is not a simple mixture of biogenic CO_2 soil gas and aquifer carbonate material. Rather, it indicates that the DIC has equilibrated to some extent with a carbon source that has relatively high values of ^{14}C and $\delta^{13}\text{C}$ such as the atmosphere. The extent of equilibration varies significantly and cannot be predicted with other well data. For the purposes of this work, ^{14}C ages have been calculated using the simple model of Vogel (1970) which assumes that the initial ^{14}C content was 85 pmc. Because the range of DIC concentration of the Group no. 1 and no. 2 samples are very similar and assuming that there is little recrystallization of

aquifer carbonate, the model ages should reflect relative age differences among the samples. However, this is not the case for the Group no. 3 samples. DIC concentrations of these samples are about a factor of 2 greater than the Group no. 1 samples, indicating that carbon has been added to the ground water. Hence, the Vogel ^{14}C ages most likely are too old. Model ages of Group no. 1, no. 2, and no. 3 samples are less than 2 kyr, 6 to 13 kyr, and greater than 23 kyr, respectively.

Cl concentrations from the Group no. 3 samples are significantly greater than observed in either Group no. 1 or no. 2 samples (Table 1) and increase systematically down gradient along our flow path. Whittemore and Fabryka-Martin (1992) have shown by examining the halogen geochemistry that the Cl source is upward migration of brine associated with Permian evaporites which lie below the Dakota aquifer in central Kansas. Assuming an end member Cl concentration similar to the maximum concentration observed in the Dakota in central Kansas, 850 mmol l^{-1} (Whittemore and Fabryka-Martin, 1992), all of the Group no. 3 samples contain less than 5% of brine fluid. Of course the percentage of brine water would be higher if the upward migrating fluid has a lower Cl concentration than assumed above.

Examination of the noble gas data reveals that in addition to Cl, the brine is enriched in He (Fig. 5). The well to well variations in the He concentration observed in the Group no. 3 samples can be largely explained with amounts of the brine that has mixed with the regional groundwater. The well data indicate that the brine has a He–Cl ratio of about $9.2 \times 10^{-7} \text{ cc STP g}^{-1}$ per mmol l^{-1} and a He concentration of about $8 \times 10^{-4} \text{ cc STP g}^{-1}$, assuming a Cl concentration of 850 mmol l^{-1} .

KGS no. 76 does not easily fit into one of the groups defined above. It is most similar to Group no. 2 samples but has higher Cl and He concentrations. It lies at the end of the flowpath near KGS no. 77 but has a lower noble gas temperature, lower ^{14}C content, and contains a larger component of the deeper brine.

4. Discussion

The chemical and isotope tracer data indicate that the different water types (Table 3) were recharged

under different conditions. This information can be used to investigate likely groundwater flow paths in the Dakota aquifer system and to establish a paleoclimate record for south-eastern Colorado. The paleoclimate record is dependent on the estimated elevation of recharge because the climate proxies (noble gas concentrations and stable isotope compositions) are both a function of long term climate change (i.e. the switching between glacial and interglacial climates) and recharge elevation. By comparing the paleoclimate record from the Dakota aquifer system with other records established from the southern United States, it is possible to determine the extent of mixing between different water types.

4.1. South-eastern Colorado wells

Two of the three water types distinguished on the basis of the tracer data, Groups no. 1 and no. 2, are found in south-eastern Colorado and adjacent areas in western Kansas (Fig. 1). The tracer data suggest a simple origin of the groundwater from the Group no. 1 wells, which are located near recharge areas in the Dakota and High Plains aquifers. The ground water from these wells recharged locally during the late Holocene. Its residence time could be as short as a few decades and is no older than a few thousand years. As mentioned above, its noble gas temperature is equivalent to the expected present day mean annual soil temperature and its $\delta^{18}\text{O}$ values range between -11.5% and -8.9% .

Relative to the Group no. 1 samples, Group no. 2 samples have lower ^{14}C contents, noble gas temperatures, and $\delta^{18}\text{O}$ values. All of these changes in the tracer data are consistent with recharge during an earlier cooler climate, such as the LGP, or at higher elevation during the early Holocene. Other significant hydrologic changes recorded in the Dakota aquifer system have been investigated by Macfarlane et al. (1997). They showed using Cl and ^{36}Cl data that the recharge rate of the Group no. 2 samples was about twice as great as that of the Group no. 1 samples.

Noble gas temperatures of the Group no. 2 samples are, on average, about 5°C cooler than the Group no. 1 samples (Fig. 6). Given the present day temperature–elevation gradient, the temperature at the maximum elevation of recharge, 1800 m, should be only 1 to 2°C cooler than in the recharge region of the Group no. 1

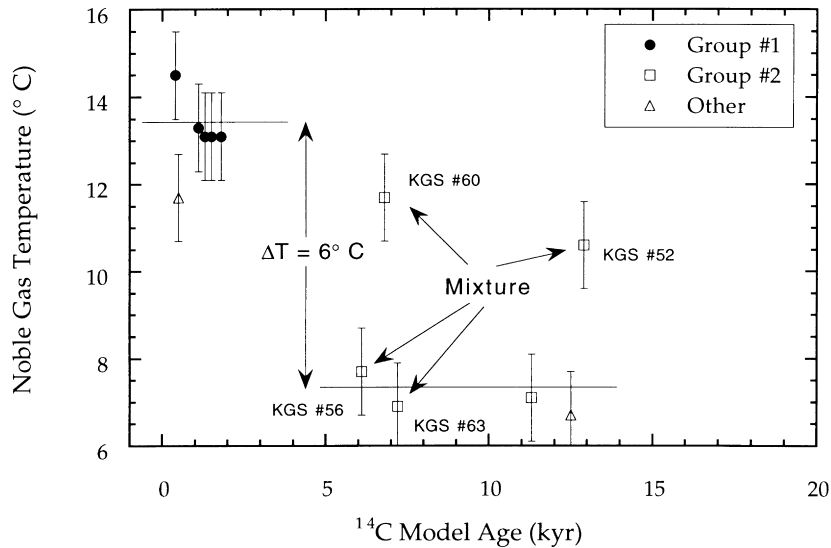


Fig. 6. Noble gas temperature plotted as a function of ^{14}C model age. ^{14}C model ages were calculated using the model of Vogel (1970). Samples which are mixtures of water recharged during the LGP and the Holocene (see text) are labeled.

wells. This implies that elevation can only contribute about one third of the observed cooling and the Group no. 2 groundwater must contain a component which was recharged during the cooler climate of the LGP.

Although the paleotemperature record (Fig. 6) from the Dakota aquifer system follows the same general trend observed in other aquifer systems from the south-western United States (Stute et al., 1992a; 1995a), there are important differences which makes it more difficult to estimate the temperature change between the Holocene and LGP in the Dakota data. However, these differences contain information, which can be used to better understand the complex flow in the Dakota aquifer system and assess mixing between different water types.

Three (KGS no. 56, 62, 63) of the five Group no. 2 samples with relatively cold noble gas temperatures suggest a cooling similar to the temperature change between the Holocene and LGP (about 6°C) found in the published records (Stute et al., 1992a; 1995a), suggesting that these samples recharged during the LGP. However, two of the Group no. 2 samples (KGS no. 52 and 60) do not show a temperature change as large ($< 3^\circ\text{C}$), and are probably mixtures of groundwater which recharged during different climates of the Holocene and the LGP. This assertion is supported in one of the samples, KGS no. 52, by the

presence of tritium and a ^{14}C content less than 18 pmc.

A simple climate change interpretation of the noble gas data is not justified for the Dakota data. First, the temperature change indicated by two samples (KGS no. 56, 63) which show about a 6°C cooling is not entirely related to climate change because these ground waters recharged at higher elevations (Table 2) where the mean annual air temperature is 1 to 2°C cooler than the temperature near the Group no. 1 wells. Hence, these samples suggest that the temperature change may have been as little as 4 to 5°C or that these samples are mixtures between water masses which recharged during different climates. Second, additional evidence for mixing can be extracted from the paleotemperature record by examining the ^{14}C data. The transition from the warm to cold noble gas temperatures occurs at about 6 kyr in the Dakota aquifer system (Fig. 6). This age is younger than what has been observed in other aquifer systems in the south-western United States. The timing of the transition is most likely a maximum because ^{14}C ages were calculated with the Vogel (1970) model and that model does not explicitly account for water–rock interactions which could lower the ages. The young ^{14}C ages (or high ^{14}C content) of the Group no. 2 samples near the temperature transition (KGS no.

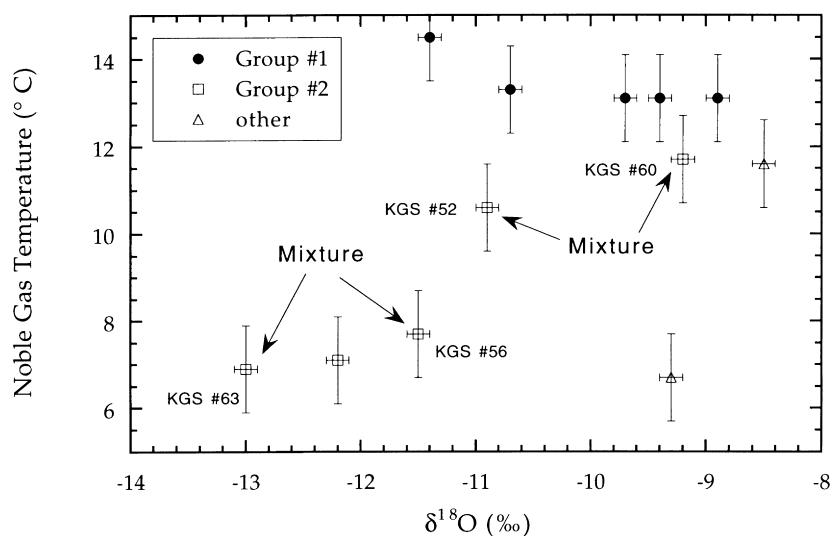


Fig. 7. Plot of noble gas temperatures as a function of $\delta^{18}\text{O}$ values. Samples which are mixtures of water recharged during the LGP and the Holocene (see text) are labeled.

56, 63) indicates that these samples have a component of young groundwater (< 30%) adding more evidence that these waters are mixtures. It is likely that there is only one sample (KGS no. 62) of the glacial end member represented in our data set. After accounting for the variations in the elevation of recharge, the Dakota aquifer data indicates that the temperature change between the Holocene and LGP was about 5°C in south-eastern Colorado, in good agreement with earlier records from the southern United States (Stute et al., 1992a; 1995a; Clark et al., 1997).

A comparison of noble gas temperatures and $\delta^{18}\text{O}$ values in south-eastern Colorado shows that the two tracers do not correlate well (Fig. 7). This indicates that recharge temperature is not the only factor that influences the stable isotope composition in the Dakota aquifer system. Here, elevation effects are equal to or greater than the effects of the 5°C temperature change associated with long-term climate change. Although in many study areas, noble gas temperatures and $\delta^{18}\text{O}$ values correlate strongly, suggesting a strong temperature dependence on stable isotope composition (M. Stute, personal communication), the dominance of geographical effects is not unique to the Dakota aquifer. This has been observed in other aquifers such as the Upper Floridan aquifer in south-eastern Georgia (Clark et al., 1997).

The composition of the excess air differs between Group no. 1 and no. 2 samples. Such a systematic change in excess air has not been reported previously. During the colder climate when recharge rates were higher (Macfarlane et al., 1997), the excess air was fractionated prior to flowing away from the water table.

4.2. Central Kansas wells

At the end of the flow path east of the Group no. 3 wells in central Kansas lie two wells which are not easily placed into any of the three water types (KGS no. 76 and 77). ^{14}C model ages of groundwater from these wells are 0.5 and 12.2 kyr and their noble gas temperatures and $\delta^{18}\text{O}$ compositions differ by about 5.3°C and 1.2‰, respectively. The tracer data indicates that this groundwater is significantly younger than the Group no. 3 wells and is part of a local flow system rather than a regional flow system, which is transporting water from higher elevation in western Kansas or south-eastern Colorado. Cl concentrations in these samples are significantly higher than the Group no. 1 and no. 2 samples but lower than the Group no. 3 samples. Helium concentrations in these samples are about an order of magnitude higher than in other samples with similar ^{14}C contents, suggesting

that the fluids carrying Cl into the aquifer are relatively old and the Cl source is from the upward migration of saline water from salt water aquifers which underlie the Dakota aquifer system.

The variation in the noble gas temperatures, $\delta^{18}\text{O}$ composition, and ^{14}C content is consistent with a climate change interpretation and implies that the glacial to interglacial change in temperature and $\delta^{18}\text{O}$ were about -5°C and -1.2‰ , respectively, in the eastern Great Plains. The differences are based on only two samples and may have a large uncertainty associated with them. However, the Holocene to LGP change in the noble gas temperature agrees well with other records from the southern United States (Stute et al., 1992a; 1995a and b; Clark et al., 1997) and with the data from south-eastern Colorado. The long-term change in $\delta^{18}\text{O}$ composition of ground waters from the southern United States varies geographically. The two closest aquifers in which both noble gases and stable isotopes have been measured are found in the San Juan Basin, New Mexico and the Carrizo aquifer, Texas. The difference between Holocene and LGP $\delta^{18}\text{O}$ compositions were about -3‰ in the San Juan Basin (Phillips et al., 1986; Stute et al., 1995a) and greater than $+1\text{‰}$ in the Carrizo aquifer (M. Stute, personal communication). The positive change in $\delta^{18}\text{O}$ composition found in the Carrizo aquifer was verified with data from the Floridan aquifer where the difference was $+0.7\text{‰}$ (Clark et al., 1997). The geographical variation in the $\delta^{18}\text{O}$ difference, apparent in ground water from the United States, is not found in Europe where LGP ground water is uniformly lower by about -1.5‰ (Rozanski, 1985). The greater geographical variation probably relates to the relatively low latitude of the United State aquifers where the stable isotope temperature effect is not as strong (Rozanski et al., 1993).

4.3. Western Kansas wells

The Group no. 3 wells are found up-gradient of KGS no. 76 and 77 and down gradient of the Group no. 1 and no. 2 wells. Ignoring any substantial water–rock interactions which would cause the Vogel ages to be too old, the ^{14}C data from the Group no. 3 wells suggest that the groundwater recharged prior to the last glacial maximum during the intermediate climate of the preceding interstadial (20 to > 50 kyr ago).

Unfortunately, noble gas recharge temperatures could not be calculated to verify these ages. The high ^{14}C content of KGS no. 71 suggests that it is a mixture of the regional and shallow groundwater.

There is evidence of mixing with a brine from the Cl and He data. As shown by Whittemore and Fabryka-Martin (1992), the high Cl concentrations are associated with upward migration of fluids which have been in contact with Permian evaporite sequences that lie below the Dakota aquifer. The fraction of brine water increases along the flow path.

Excluding KGS no. 68 and no. 71 (which appears to be mixture based on its ^{14}C content), the Group no. 3 samples have a very small range in $\delta^{18}\text{O}$ values (-12.1‰ to -11.7‰). This suggests that either the groundwater was recharged during a period of small climate variations at approximately the same elevation or dispersion has removed the climate and elevation information. Other conservative tracers which were supplied to the groundwater system at the time of recharge, such as the noble gases, also show small variations. Stute and Schlosser (1993) have shown that climate signals are preserved in most sandstone aquifers with residence times on the order of 10^4 years or less, suggesting that dispersion does not significantly affect the composition of ground water on these time scales. The data from south-eastern Colorado supports their finding. However, Musgrove and Banner (1993) determined that mixing exerts significant controls on the composition of regional ground water from deep aquifers in the mid-continent which probably have ground water residence times of 10^6 years or longer. The spatial scale of flow in the confined Dakota is between that found in south-eastern Colorado and the mid-continent aquifers examined by Musgrove and Banner (1993). To what extent dispersion is influencing the $\delta^{18}\text{O}$ composition of ground water in the confined Dakota can not be determined from the geochemical data alone and requires further study.

Dutton (1995) suggested that the low $\delta^{18}\text{O}$ waters found in the Dakota aquifer system in western Kansas recharged locally during a colder climate and infiltrated into the confined Dakota via vertical leakage through the overlying aquitard. Shallow ground water found near this area in western Kansas has an average $\delta^{18}\text{O}$ content of -9.4‰ (Table 2; Dutton, 1995), about 2.6‰ heavier than the water from the confined Dakota. The difference in $\delta^{18}\text{O}$ between the

shallow and confined ground water in central Kansas is greater than the glacial to interglacial change inferred from KGS no. 76 and no. 77. Thus, a component of this water must have recharged at higher elevations, presumably in south-eastern Colorado or extreme western Kansas. The isotope data cannot be used to exclude the possibility that the ground water in the confined Dakota is a mixture of water, which recharged at very different elevations. However, because it seems unlikely that the proportion of each of these water masses would be the same at all of the Group no. 3 wells, the simplest explanation is that the ground water in the confined aquifer recharged at higher elevations, probably near the Arkansas River valley and flowed down gradient to central Kansas.

5. Summary

The study demonstrates the importance of using multiple tracers when investigating the flow systematics and climate records archived in ground water systems. Multiple tracers are needed to separate the effects of mixing of water masses with different histories presumably caused by wells with large screen intervals. Despite the mixing, three distinct water types can be identified on the basis of the chemical and tracer data in the Dakota aquifer in south-eastern Colorado and western and central Kansas. The origin of the three water types implies a flow pattern which is similar to the one suggested by Macfarlane (1995). Two of the three water types are found in south-eastern Colorado. Group no. 1 samples were found at shallower depths, had groundwater residence times on the order of 10^2 – 10^3 yr, and had noble gas temperatures which were consistent with the local present day mean annual air temperature. Group no. 2 samples had groundwater residence times on the order of 10^4 yr and noble gas temperatures about 4–6°C cooler. Relative to the Group no. 1 samples, Group no. 2 samples recharged at higher elevations during the LGP. The paleotemperature record derived from this data suggest that south-eastern Colorado was about 5°C cooler during the LGP. A similar temperature change has been previously reported from aquifer data for north-western New Mexico and southern Texas (Stute et al., 1992a; b; 1995a). The third water type was found in central and western Kansas.

It represents the regional groundwater flow through the confined Dakota aquifer. This water was most likely recharged near the Arkansas River valley at elevations significantly higher than the well heads and has residence time on the order of 10^4 to 10^5 yr. The tracer data also indicate that a deeper brine is mixing into this water mass. Two samples collected down gradient of the Group no. 3 wells were significantly younger, indicating that local groundwater flow systems penetrate the Dakota aquifer system in Central Kansas near the discharge area of the regional flow system. Data from these wells suggest that the glacial to interglacial change in $\delta^{18}\text{O}$ in the central Great Plains of the United States was about –1.2%.

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